Book Reviews

Organohalosilanes. Precursors to Silicones. By R. J. H. Voorhoeve, Research Chemist, Koninklijke/Shell-Laboratorium, Amsterdam, The Netherlands. American Elsevier Publishing Co., Inc., 52 Vanderbilt Ave., New York, N. Y. 1967. xiv + 423 pp. 16 × 23 cm. $25.00.

The general reaction of organic halides with silicon to yield organohalosilanes was first reported by E. G. Rochow in 1945 and is usually referred to as "the direct synthesis." The latter comprises one of the most important synthetic methods for organosilicon compounds. Indeed, the direct synthesis of methylhalosilanes (Me_2SiCl_2, Me_3SiCl, $MeSiCl_3$) from methyl chloride and silicon is the most widely used industrial method for the preparation of organosilicon monomers which then are converted by hydrolysis and other reactions into silicones having useful and unusual properties.

Almost 20 years after the discovery of the direct synthesis, the author of this book received the doctor's degree from the Technical University of Delft, where he completed a thesis in 1964 entitled, "Mechanism and Technology of the Synthesis of Methylchlorosilanes."

During the past decade the great rate of expansion of effort and interest in the organosilicon field has led to the writing of several books concerning various aspects of this large subject. The unique contribution of the present book lies in its detailed treatment (130 pp) of the direct synthesis in Chapters 4, 5, 6, 7, and 8 entitled, respectively, General Principles of the Direct Synthesis of Methylhalosilanes and Other Organohalosilanes, Laboratory Synthesis of Methylchlorosilanes in Fluidized Beds, Direct Synthesis of Organohalosilanes Containing No Methyl Groups, Kinetics of the Direct Synthesis, and Mechanism of the Copper-Catalyzed Reactions between Silicon and Organic Halides. The mechanistic conclusions of Dr. Voorhoeve concerning the selective formation of diorganodihalosilanes are summarized at the end of Chapter 8. Although some of these are not capable of very direct experimental proof, the more general features of these conclusions seem quite reasonable to this reviewer. Thus, a first step involving dissociative chemisorption of methyl chloride on the polarized surface ($Si^{\delta -}$–$Cu^{\delta +}$) of a Si–Cu alloy seems well established. In this step the organic group becomes attached to the silicon and the halogen to the copper. This step is postulated to be followed by a rate-determining step involving nucleophilic attack by a chloride ion (from $Cu^{\delta +}$–$Cl^{\delta -}$) on a silicon–substrate bond. Involvement of two methyl chloride molecules, a single silicon center, and two copper centers can thus lead to formation of Me_2SiCl_2.

In addition to its excellent and detailed treatment of the direct synthesis of organohalosilanes, the book contains chapters dealing with other synthetic methods for these compounds, their chemical and physical properties, and some industrial aspects and applications involving organohalosilanes and their derivatives. The book concludes with a chapter on the analysis of organohalosilanes.

Considering the importance of organohalosilanes in organosilicon chemistry this book should prove useful to chemists working with the industrial or academic aspects of the subject. In addition, chemists interested in the field of catalytic phenomena and the reactions of solids should find the chapters on the direct synthesis of some interest.

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Spectroscopy and Structure of Metal Chelate Compounds. By Kazuo Nakamoto, Illinois Institute of Technology, and Paul J. McCarthy, S. J., Canisius College. John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1968. xi + 382 pp. 16 × 23.5 cm. $16.95.

This is one of the latest in a series of rather specialized books recently published which deal with the reactions, stereochemistry, and electronic structures of transition metal complexes. As the title suggests, discussion is completely confined to chelate complexes. The spectroscopic methods treated are X-ray and neutron diffraction, visible and ultraviolet spectroscopy, optical rotatory dispersion and circular dichroism, infrared spectroscopy, electron paramagnetic resonance, and nuclear magnetic resonance.

The volume is divided into six chapters on the above subjects. Of these Chapter 1 on X-ray and neutron diffraction by Y. Saito and Chapter 3 on ORD and CD by J. Fujita and Y. Shimura are particularly worthwhile. Saito's contribution includes a description of the methodology of structure solution by the diffraction methods together with several brief examples. Also included is a comprehensible description of the principle of absolute configuration determination by anomalous dispersion of X-rays and a resumé of some of the more important chelate structures solved in the last half-dozen years. Chapter 3 contains a brief but useful introduction to ORD and CD theory followed by a section on applications which places the expected emphasis on determination of absolute configurations of cobalt(III) complexes. This section is not completely up to date but nonetheless serves as a reasonable introduction to the way in which ORD and CD are currently used in establishing relative and absolute configurations of complexes. Chapter 2 on ultraviolet and visible spectroscopy by C. R. Hare provides a workmanlike introduction to simple ligand field theory including reproduction of the Tanabe–Sugano energy diagrams for the d^2–d^8 octahedral cases. The emphasis throughout is, of course, on lower symmetry fields such as trigonal and tetragonal, and these cases, together with those arising from pseudotetrahedral, planar four-coordinate, and five coordinate geometries are considered by means of a series of well-chosen examples from the recent literature. The various forms of semiempirical molecular orbital theory currently applied to spectral interpretations are afforded little consideration, but limited references to some of the more important papers are provided. Infrared spectroscopy by K. Nakamoto is treated in Chapter 4, which contains a capsule description of normal coordinate analysis followed by examples of structural determinations, many of which are taken from the author's own work. This chapter is best described as an updating of the author's well-known test of 5 years ago on the infrared spectra of coordination compounds, with emphasis here on the application of the method to chelate complexes. Epr spectroscopy is dealt with in Chapter 5 by S. Fujiwara. This chapter is not satisfactory for any obvious purposes. The theoretical development, even at the simplest level, is incomplete and the applications deal only with d^1 and d^9 cases. The tabulation of reported epr studies on metal chelates is also incomplete, and whatever value it might otherwise have is vastly reduced by the unfortunate practice of listing references in terms of metal and oxidation state rather than by individual complexes. The final chapter, by P. J. McCarthy, S. J., is a largely uncritical description of the applications of nmr to problems of structure and bonding. The emphasis is on kinetically stable diamagnetic and paramagnetic complexes. Most of the important work in this area within the last half-dozen years or so is covered briefly and the chapter is liberally referenced.

Because this book is not intended, and, indeed, does not serve, as a satisfactory theoretical introduction to the various spectroscopic methods considered, its principal value must derive from the applications of these methods. With the exception of ORD and CD, there seems little to be gained by restricting applications of the spectroscopic methods to chelates alone out of the entire body of coordination compounds, despite the authors' desire to maintain the volume of material "tractable." In short, this book as a whole fulfills no particular need and, consequently, is not likely to enjoy widespread use, even among the specialists in chelate chemistry who probably will not choose to pay the substantial price involved for a catalog of spectroscopic applications.

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